Final Report for Period: 03/2008 - 02/2009
Submitted on: 03/04/2009
Principal Investigator: Bunz, Uwe H.
Award ID: 0548423
Organization: GA Tech Res Corp - GIT
Submitted By:
Bunz, Uwe - Principal Investigator
Title:
Heteroacenes

Project Participants

Senior Personnel

Name: Bunz, Uwe
Worked for more than 160 Hours: Yes
Contribution to Project:

Post-doc

Name: Miao, Shaobin
Worked for more than 160 Hours: Yes
Contribution to Project:
Synthetic chemistry, postdoc; developed syntheses of peralkynylated heteroacenes

Graduate Student

Name: Brombosz, Scott
Worked for more than 160 Hours: Yes
Contribution to Project:
2nd year graduate student. Is synthesizing donor-substituted heteroacenes and ionic heteroacenes

Name: McGrier, Psaras
Worked for more than 160 Hours: Yes
Contribution to Project:
African American 2nd year graduate student, synthesizes phenolate-substituted donor-acceptor heteroacenes and benzothiadiazoles.

Name: Appleton, Anthony
Worked for more than 160 Hours: Yes
Contribution to Project:
Synthesis of novel heteroacenes

Name: Berger, Nancy
Worked for more than 160 Hours: No
Contribution to Project:
Synthesis of precursors. Nancy is a first year graduate student

Undergraduate Student

Name: Zappas, Drew
Worked for more than 160 Hours: Yes
Contribution to Project:
Has worked on synthesis and characterization of novel heteroacenes

Name: Wang, Donnie

Worked for more than 160 Hours: Yes

Contribution to Project:
Has worked on the synthesis and characterization of novel precursors for peralkynylated heteroacenes

Technician, Programmer

Other Participant

Name: Ramsey, Andrew

Worked for more than 160 Hours: Yes

Contribution to Project:
Andrew has a BS in Materials Science and investigates the formation of microcrystalline materials and thin films of heteroacenes on coated glass, quartz and indium tin oxide slides

Research Experience for Undergraduates

Organizational Partners

Other Collaborators or Contacts

Paul M. Berger, Electrical Engineering, Ohio State
David VandenBout, Chemistry, U of Texas
Dvora Perahia, Chemistry, Clemson
Seth R. Marder, Chemistry, Georgia Institute of Technology
Bernard Kippelen, Electrical Engineering, Georgia Institute of Technology
Cliff Henderson, School of Chemical Engineering, Georgia Institute of Technology

Activities and Findings

Research and Education Activities:
see attached file for research activities.
For educational activities, the PI has taught in the Fall of 07 the Course 'Advanced Organic Chemistry' as an advanced undergraduate class at Clark Atlanta University.

The PI has established a strong interaction with Tri-Cities High School (TCH), a minority inner city high school in South Atlanta. One of the PI's graduate students, Ronnie Phillips has been a STEP fellow for a year and taught honors chemistry at TCH. As a consequence we have had (and have!) a significant number of high school students (HS) in my laboratory, exposing cruciforms to different analytes. These high school students work mainly in combination with graduate students and have measured UV-vis and emission spectra. These activities do are non-hazardous yet foster understanding and interest in chemistry. At the same time, the HS have gathered real data on a real research instrument and learned the culture of a real research laboratory. These activities taught the HS to work carefully. This summer we have had Margret Tarver (chemistry high school teacher) and three of her students (Alando Wilson [African American], Diana Vazquez [Hispanic], Daunia Martinez [Hispanic]) from TCH working in my laboratory. A publication in Organic Letters has resulted from this work.

Findings: (See PDF version submitted by PI at the end of the report)
see attached file, see above

Training and Development:
see above; several graduate students and undergraduate students have worked on the project and obtained training.

Outreach Activities:
see attached report file, see above

Journal Publications

Miao S. B.; Smith, M. D.; Bunz, U. H. F., "Synthesis of a peralkynylated pyr¬a¬zino[2,3-g]quinoxaline", Organic Letters, p. 757, vol. 8, (2006). Published,

Miao, S.; Schleyer, P. v. R.; Wu, J. I.; Hardcastle, K. I.; Bunz, U. H. F.
, "A Thiadiazole-Fused N,N-Dihydroquinoxaline: Antiaromatic but Isolable
", Org. Lett., p. 1073, vol. 9, (2007). Published,

Wang, Y.; Park, J. S.; Leech, J. P.; Miao, S.; Bunz, U. H. F.
, "Poly(aryleneethynylene)s with Orange, Yellow, Green, and Blue Solid-State Fluorescence
", Macromolecules, p. 1843, vol. 40, (2007). Published,

Scott M. Brombosz, Anthony J. Zucchero, Ronnie L. Phillips, Diana Vazquez, Alando Wilson and Uwe H. F. Bunz, "Terpyridine-Based Cruciform-Zn2+ as Anion-Responsive Fluorophores", Organic Letters, p. 4519, vol. 9, (2007). Published,

Miao, S; Brombosz, SM; Schleyer, PV; Wu, JI; Barlow, S; Marder, SR; Hardcastle, KI; Bunz, UHF, "Are N,N-dihydrodiazatetracene derivatives antiaromatic?", JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, p. 7339, vol. 130, (2008). Published, 10.1021/ja077614

McGrier, PL; Solntsev, KM; Miao, S; Tolbert, LM; Miranda, OR; Rotello, VM; Bunz, UHF, "Hydroxycruciforms: Amine-responsive fluorophores", CHEMISTRY-A EUROPEAN JOURNAL, p. 4503, vol. 14, (2008). Published, 10.1002/chem.20080029

Shaobin Miao, Anthony L. Appleton, Nancy Berger, Stephen Barlow, Seth R. Marder, Kenneth I. Hardcastle, Uwe H. F. Bunz, "6,13-Diethynyl-5,7,12,14-tetraazapentacene", Chemistry a European Journal, p. , vol. , (2009). Accepted,

J. I. Wu, C. S. Wannere, Y. Mo, P. v. R. Schleyer, U. H. F. Bunz, "4n ð Electrons but Stable: N,N-Dihydrodiazapentacenes", Journal of the American Chemical Society, p. , vol. , (2009). Submitted,

Hauck, M; Schonhaber, J; Zucchero, AJ; Hardcastle, KI; Muller, TJJ; Bunz, UHF, "Phenothiazine cruciforms: Synthesis and metallochromic properties", JOURNAL OF ORGANIC CHEMISTRY, p. 6714, vol. 72, (2007). Published, 10.1021/jo070922

Books or Other One-time Publications

Web/Internet Site

Other Specific Products

Contributions

Contributions within Discipline:

Development of new synthetic methods to prepare acceptor-based alkynylated heteroacenes.
Synthesized a series of novel heteroacenes and larger thiadiazoles.

Contributions to Other Disciplines:

The synthesized materials are of importance as amine-sensors and as potential n-semiconductors for photovoltaics

Contributions to Human Resource Development:

Contributions to Resources for Research and Education:

see discussion in the activities and finding section

Contributions Beyond Science and Engineering:

Categories for which nothing is reported:

Organizational Partners
Any Book
Any Web/Internet Site
Any Product
Contributions: To Any Human Resource Development
Contributions: To Any Beyond Science and Engineering

Annual Report
Heteroacenes (NSF CHE 0548423)

PI: Prof. Uwe Bunz,
School of Chemistry and Biochemistry, Georgia Institute of Technology
Reporting Period March 2007-March 2008

Introduction

The higher acenes are spectacularly successful in organic electronics, due to their high charge carrier mobility.[1] Pentacene in particular is most useful for applications in thin film transistors.[2] Its crystal packing imparts significant $\pi-\pi$ intermolecular overlap resulting in an organic semiconductor in the solid state.[2,3] Anthony has demonstrated that pentacenes, hexacenes, and heptacenes with strategically placed, sterically demanding alkyne substituents are stable and easily processed.[3] Their crystal structures can be manipulated predictably by the choice of appropriate substituents to maximize $\pi-\pi$-stacking in the solid state.[4] We now explore the potential extension of these capabilities by synthesizing and studying the properties of a pair of soluble and redox-related diaza and dihydrodiaza hetero-tetracenes.[5,6,7,8,9,10,11] Large heteroacenes show potential as n-semiconductors. We have made considerable progress in three subfields concerning the synthesis and property evaluation of larger heteroacenes.

1) Aromaticity and Antiaromaticity of Larger Heteroacenes

2) Synthesis of and Structural Characterization of a heterocyclic heptacene

3) Synthesis and Property Evaluation of Larger Acenothiadiazoles

1) Aromaticity and Antiaromaticity of Larger Heteroacenes

An underappreciated and rarely discussed aspect of the chemistry of the larger diazaacenes is their reduction (hydrogenation) to their formally antiaromatic congeners (Scheme 1). Indeed, the dihydro-forms of the diaza- and tetraazapentacenes often seem to be remarkably viable.[4] Hinsberg reported that both the parent and the dihydro forms of diaza- and tetraazatetracenes were persistent, and he contended that the dihydro forms of the larger azaacenes were even more stable.[12] The notions of aromaticity and particu- larly of antiaromaticity[13] were not

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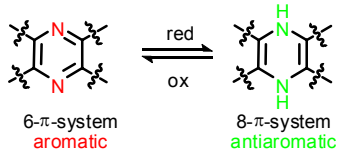
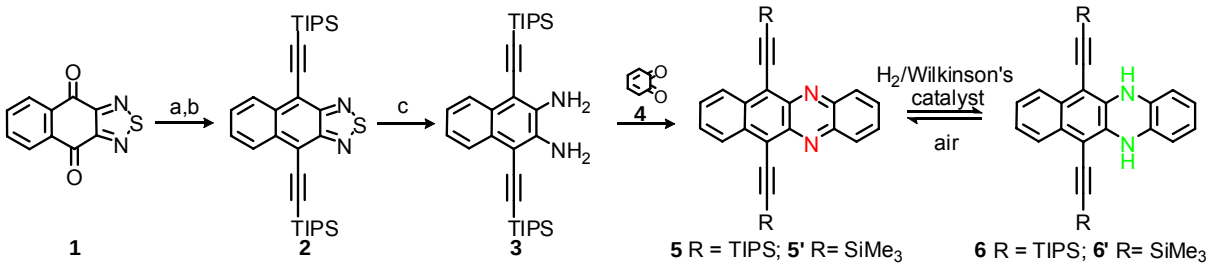
[1] Nelson, S. F.; Lin, Y. Y.; Gundlach, D. J.; Jackson, T. N. *Appl. Phys. Lett.* **1998**, *72*, 1854-1856.
[2] (a) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater*. **2002**, *14*, 99-117. (b) Dimitrakopoulos, C. D.; Mascaro D. J. *IBM J. Res. Develpment* **2001**, *45,* 11-27. (b) Reese, C.; Bao, Z. N. *J. Mater. Chem.* **2006**, *16*, 329-333. (d) Roberson, L. B.; Kowalik, J.; Tolbert, L. M.; Kloc, C.; Zeis, R.; Chi, X. L.; Fleming, R.; Wilkins, C. *J. Am. Chem. Soc.* **2005**, *127* , 3069-3075.
[3] (a) Anthony, J. E. *Chem. Rev.* **2006,** *106*, 5028-5048. (b) Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 9482-9483. (c) Payne, M. M.; Parkin, S. R.; Anthony J. E. *J. Am. Chem. Soc.* **2005**, *127*, 8028-8029.
[4] Anthony, J. E.; Eaton, D. L.; Parkin, S. R. *Org. Lett.* **2002**, *4*, 15-18.
[5] (a) Fischer, O.; Hepp, E. *Chem. Ber.* **1890**, *23*, 2789-2798.(b) Fischer, O.; Hepp, E. *Chem. Ber.* **1900**, *33*, 1485-1498. (c) Kehrmann, F. *Chem. Ber.* **1890**, *23*, 2446-2454.
[6] Winkler, M.; Houk, K. N. *J. Am. Chem. Soc.* **2007**, *129*, 1805-1815.
[7] Wudl, F.; Koutenis, P. A.; Weitz, A.; Ma, B.; Strassner, T.; Houk, K. N.; Khan, S. I. *Pure Appl. Chem.* **1999**, *71*, 295-302.
[8] Miao, Q.; Nguyen, T. Q.; Someya, T.; Blanchet, G. B.; Nuckolls C*. J. Am. Chem. Soc.* **2003**, *125*, 10284-10287.
[9] Tadokoro, M.; Yasuzuka, S.; Nakamura, M.; Shinoda, T.; Tatenuma, T.; Mitsumi, M.; Ozawa, Y.; Toriumi, K.; Yoshino, H.; Shiomi, D.; Sato, K.; Takui, T.; Mori, T.; Murata, K. *Angew. Chem.* **2006**, *45*, 5144-5147.
[10] Jenekhe, S. A.; *Macromolecules* **1991**, *24*, 1-10
[11] Nishida, J.; Naraso; Murai, S.; Fujiwara, E.; Tada, H.; Tomura, M.; Yamashita, Y. *Org Lett.* **2004,** *6*, 2007-2010.
[12] Hinsberg, O. *Liebigs Ann. Chem.* **1901**, *319*, 257-286.
[13] Breslow, R.; Brown, J.; Gajewski J. J. *J. Am. Chem. Soc.* **1967**, 89, 4383-4390.

developed in 1901. Consequently, the behavior of the formally antiaromatic dihydronaphtho-phenazine did not seem surprising at the time. This contribution illuminates the stabilities and spectroscopic properties of **5** and **6** in relationship to their aromatic/antiaromatic character.



Scheme 1. Interconversion of an aromatic 6-π-pyrazine module into an antiaromatic 8-π-dihydropyrazine module.



Scheme 2. Synthesis of the heteroacene **5** and dihydroacene **6**. a: Tips-CC-Li, then wet ether; b: KI, NaH_2PO_2, AcOH, c: $LiAlH_4$, THF.

The diol, formed by addition of the lithium salt of triisopropylsilylacetylene to quinone **1**,[14] reacts with potassium iodide and sodium hypophosphite in acetic acid to give the naphthothiadiazole derivative **2** (87%).[15] $LiAlH_4$ reduction of **2** in THF afforded diamine **3** (98%) as a blue-fluorescent, almost colorless powder. *ortho*-Quinone (**4**), obtained by oxidation of catechol in dichloromethane by acidic aqueous dichromate, was coupled with **3** to furnish **5** (63%) after flash chromatography (hexanes/dichloromethane 1/1) as dark-red, air-stable, crystalline material.

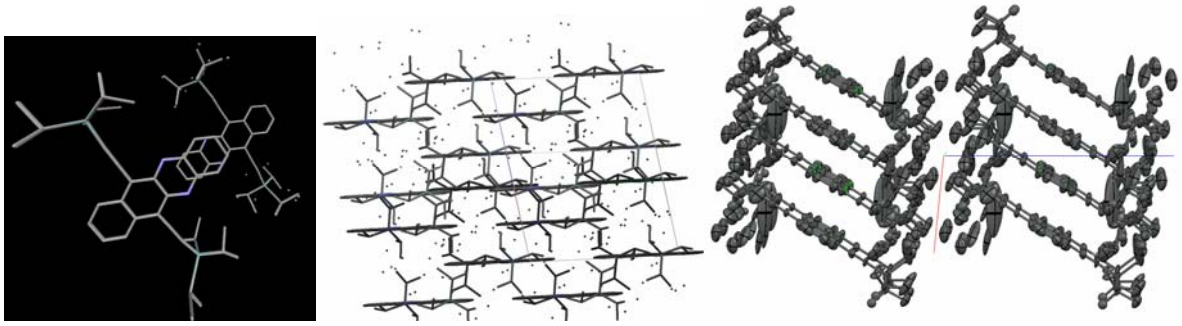


Figure 1. Packing of **5**. View of molecules stacked on top of each other. The distance between the planes of the two molecules is 3.35 Å. Parallel alignment of the stacks along the *b*-axis (right)

The topology of **5** and its solid-state packing (Figures 1) were obtained by X-ray analysis of a crystal grown from hexanes/dichloromethane solution. Heteroacene **5** packs in a 2-D-stack but with significant short-axis offset, similar to acceptor-substituted tetracene derivatives prepared by Anthony et al.[16] The short intra-stack distance of two molecules of **5**, 3.35 Å, equals the

[14] Cava, M. P.; Schlessinger, R. H. *Tetrahedron Lett.* **1964**, 3815-3817.
[15] Miao, S.; Smith, M. D.; Bunz, U. H. F. *Org. Lett.* **2006**, *8*, 757-760. (b) Miao, S.; Schleyer, P. v. R.; Wu, J. I.; Hardcastle, K. I.; Bunz U. H. F. *Org. Lett.* **2007**, *9*, 1073-1076.
[16] (a) Odom, S. A.; Parkin, S. R.; Anthony, J. E. *Org. Lett.* **2003**, *5*, 4245-4248. (b) Anthony J. E. in Functional Organic Materials, Ed. Bunz U. H. F., Müller T. J. J., Wiley-VCH, Weinheim **2007**, 511-545.

combined van der Waals radii of carbon, and might lead to efficient charge transport in the solid state.

While 6,11-bis(triisopropylsilylethynyl)benzo[b]phenazine (**5**) is non-fluorescent in the solid state due to its intra-stack interactions, it is red-fluorescent in solution with acene-type patterns both in absorption and emission (λ_{max} abs = 571 nm, λ_{max} emission = 583 nm);[17] **5** is persistent and melts at 186°C without decomposition. It can be hydrogenated at 2500 psi H_2 pressure using Wilkinson's catalyst ($(Ph_3P)_3RhCl$) to give a new, brightly yellow-green fluorescent compound (assigned structure **6**) in 98% yield. The absorption and emission spectra of **6** are shown in Figure 2 (λ_{max} abs = 482 nm, λ_{max} emission = 491 nm). The NH units gave a distinct, sharp IR band at 3396 cm^{-1} and a single broad ^1H NMR peak. Otherwise, the NMR spectrum of **6** is similar to that of **5**, except that all the ^1H signals are shifted to higher field. Dihydro-heteroacene **6** is isolable but reverts quickly to **5** on exposure to air, both in solution and in the solid state. Interestingly, the acetylene substituents seem to decrease the persistence of **6**, compared to Hinsberg's parent diazadihydrotetracene **6''**.[12]

Despite the formally 4n-π-antiaromatic character of **6**, **6'**, and **6''**, the computed heat of hydrogenation of **5''** to **6''** (ΔH_H = -20.8 kcal/mol at B3LYP/6-311+G** with ZPE correction) is actually 5.8 kcal/mol more exothermic than that of the inner ring of tetracene (ΔH_H = -15.0 kcal/mol), *suggesting that **6''** is destabilized only modestly by its antiaromatic dihydropyrazine ring.*

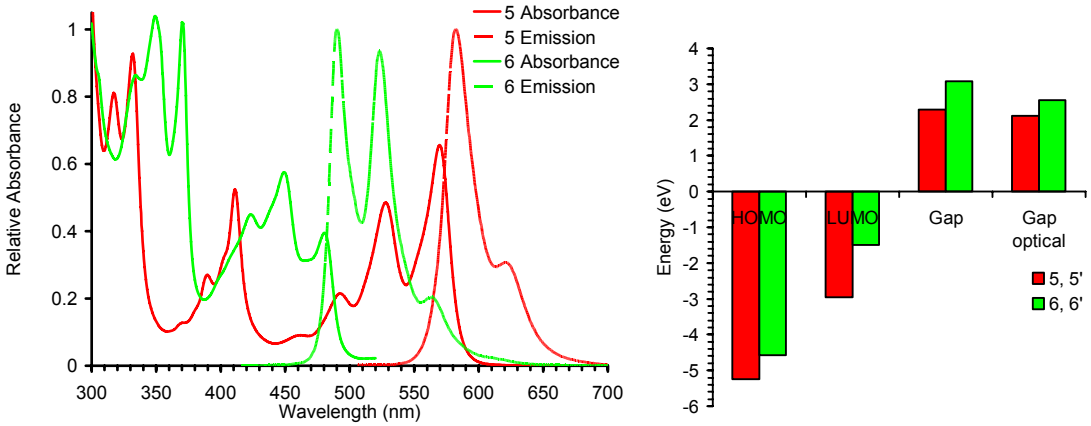


Figure 2. Normalized UV-vis and emission spectra of **5** and **6** in dichloromethane (Left). HOMO and LUMO positions from quantum chemical calculations for **5'** and **6'** (B3LYP/6-31G*) and HOMO-LUMO gap from calculations (Gap) and from the optical data (Gap optical) for **5** and **6** (Right).

5'' + H_2 → **6''** ΔH_H = -20.8 kcal/mol

Tetracene + H_2 → 5,12-Dihydrotetracene ΔH_H = -15.0 kcal/mol

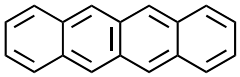
Moreover, this comparison is influenced by the difference in CH vs. NH bond energies. Thus, the computed heat of hydrogenation involving nonaromatic models, 2,3-dihydropyrazine, to 1,2,3,4-tetrahydropyrazine (ΔH_H= -18.8 kcal/mol) is nearly the same as **5''** to **6''** whereas the hydrogenation of 2,3-cyclohexadiene to cyclohexene (ΔH_H= -22.5 kcal/mol) is 7.5 kcal/mol more exothermic than that of tetracene to dihydrotetracene. Consequently, **5''** actually looses less aromatic stabilization energy than tetracene upon hydrogenation, despite the 4n-π-electron character of **6''**.

The HOMO-LUMO gap of *aromatic* **5** is smaller than that of the *formally antiaromatic* **6**. Figure 2 compares the computed HOMO and LUMO energies as well as the computed and

[17] Perkampus H.-H. UV-Vis Atlas of Organic Compounds, 2nd ed. VCH, Weinheim 1992.

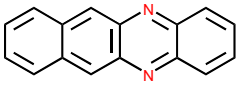
experimental band gaps (the latter were obtained from the intersection of absorption and emission traces). The calculated HOMO energy increases from -5.2 eV for **5'** to -4.6 eV for **6'**, but the difference in LUMO energies is greater (-3.0 eV for **5'** vs. -1.5 eV for **6'**). As a consequence, the band gap increases from 2.3 eV for **5'** to 3.1 eV in **6'**. The experimentally obtained optical band gaps for **5** and **6** (2.1 eV and 2.6 eV, respectively) agree reasonably well.

Diazatetracenes, like **5**, certainly are aromatic, but what is the nature of their dihydro derivatives? Is **6** really antiaromatic? NICS (nucleus independent chemical shifts) computations at the centers of the individual rings of the parent systems, **5"** and **6"**, as well as tetracene for comparison are revealing (Figure 3).[18] Our analysis employs the sophisticated NICS(0)$_{\pi zz}$ index,[19] which is based on the out-of-plane tensor components of both the canonical (CMO)



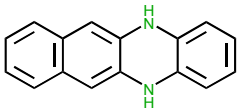
tetracene

LMO					
Remote	-1.6	-3.4	-	-	$\Sigma NICS(0)_{zz}$ = -10.0
Local	-28.4	-39.2	-	-	$\Sigma NICS(0)_{zz}$ = -135.2
Total	-30.0	-42.6	-	-	$\Sigma NICS(0)_{zz}$ = -145.2
CMO					
Total	-29.6	-42.1	-	-	$\Sigma NICS(0)_{zz}$ = -143.4



5"

LMO					
Remote	-2.0	-3.8	-3.6	-2.8	$\Sigma NICS(0)_{zz}$ = -12.2
Local	-28.0	-39.1	-38.2	-27.9	$\Sigma NICS(0)_{zz}$ = -133.2
Total	-30.0	-42.9	-41.8	-30.4	$\Sigma NICS(0)_{zz}$ = -145.4
CMO					
Total	-30.0	-42.5	-41.1	-30.1	$\Sigma NICS(0)_{zz}$ = -144.0



planar **6"**

LMO					
Remote	7.9	15.1	2.1	15.7	$\Sigma NICS(0)_{zz}$ = 40.8
Local	-35.1	-29.9	27.6	-33.4	$\Sigma NICS(0)_{zz}$ = -70.8
Total	-27.2	-14.8	29.7	-17.7	$\Sigma NICS(0)_{zz}$ = -30.0
CMO					
Total	-26.3	-14.2	31.3	-16.7	$\Sigma NICS(0)_{zz}$ = -25.9

Figure 3. IGLO-LMO (localized molecular orbital) and GIAO-CMO (canonical molecular orbital) NICS(0)$_{\pi zz}$ computed at PW91/IGLO-III//B3LYP/6-311+G**. "Local" refers to the π LMO contributions of individual localized double bonds and lone pairs associated with the designated individual rings (when appropriate, localized exocyclic π bonds are included). "Remote" refers to the remaining π MO contributions. Note also that the sum of the remote and local total LMO contributions matches the CMO total closely. (The planar C_{2v} form of **6"** had one imaginary frequency, but essentially the same energy as the C_s minimum).

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[18] (a) Schleyer, P. V. R.; Maerker, C.; Dransfeld, A.; Jiao, H. J.; Hommes, N. J. r. V. E. *J. Am. Chem. Soc.* **1996**, 118, 6317-6318.

[19] (a) Corminboeuf, C.; Hein, T.; Seifert, G.; Schleyer, P. v. R. *J. Phys. Chem. Chem. Phys*. **2004**, 6, 273-276. (b) Chen, Z. F.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Chem. Rev.* **2005**, *105*, 3842-3888. (c) Fallah-Bagher-Shaidaei, H.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Org. Lett.* **2006**, *8*, 863-866.

and the localized (LMO) π molecular orbital contributions to the isotropic NICS. $NICS(0)_{\pi zz}$ data for both the dissected IGLO-LMO method (with Pipek-Mezey localization as implemented in the deMon program)[20,21] and the GIAO-CMO[22] method are computed at PW91/IGLO-III//B3LYP/6-311+G** for uniformity.

As expected, all the individual local $NICS(0)_{\pi zz}$ values of **5''** and the overall $\Sigma NICS(0)_{\pi zz}$ sums are highly diatropic and are similar to those of tetracene (Figure 5 top and middle structures).[23] Both their total LMO and total CMO $NICS(0)_{\pi zz}$ data are almost identical. The LMO details are instructive. They reveal that that the large negative $NICS(0)_{\pi zz}$ values of the individual rings are due to their "local" diatropicity (i.e., the π contributions involving each ring itself). The "remote" π contributions (from the other rings) are rather small. In this sense, the diamagnetic contributions of the aromatic subunits of both **5''** and tetracene are localized. This is in line with Clar's rule that structures with a maximum number of localized sextet rings are advantageous energetically. Hence, $NICS(0)_{\pi zz}$ is a relatively uncontaminated measure of the magnetic aromaticity of individual rings in a polycyclic aromatic system. The inner rings of **5"** and of tetracene are more diatropic than the outer rings.[23]

Remarkably, the behavior of the formally "antiaromatic" dihydro **6"** is quite different. The total NICS sums, $\Sigma NICS(0)_{\pi zz}$ = -28±2 for LMO and CMO, indicate **6"** to be *weakly aromatic* despite its 4n-π-perimeter (Figure 5, bottom structure). For comparison, the total NICS sums, $\Sigma NICS(0)_{\pi zz}$, of tetracene and of **5"** (both ca -145) are much larger in magnitude. The dihydropyrazine ring in **6"** is strongly paratropic, as expected, but its "antiaromatic" contribution to the whole molecule is overwhelmed by the diatropicity of the other, carbocyclic rings in **6"**, which are aromatic. Note that the paramagnetic contribution of the dihydropyrazine ring in **6"** is *delocalized*. Unlike **5"**, the "remote" LMO contributions of the individual aromatic rings of **6"** (shown in green) are distinctly paratropic. As a consequence, the diatropicity (aromaticity) of the two rings adjacent to the dihydropyrazine ring in **6"** are both reduced significantly to $NICS(0)_{\pi zz}$ total = -14.2 to -17.7, much lower when compared to the ca -30 to -42 range for the corresponding rings of **5"** and of tetracene (Figure 3).

In conclusion, we have prepared a redox interconvertible pair of heterocyclic tetracene derivatives, the aromatic **5** and its dihydro-derivative **6**. Both compounds are potentially useful as active layers in thin film transistors. While **5** is persistent, **6** is readily oxidized to **5** in air. Aromatic **5** with 18 π electrons has a small band gap and is red-fluorescent. Its reduced dihydro counterpart **6** is green-fluorescent and has a significantly larger band gap. Despite having 20 π electrons, **6** is net aromatic, rather than antiaromatic. The paratropicity resulting from the anti-aromatic (4n-π) dihydropyrazine subunits is *delocalized*. For this reason, large 4n π compounds like **6, 6'** or **6"** do not become antiaromatic. The "antiaromaticity" contribution of an individual ring is diffused over the whole system. Thus **6"** and therefore **6** are overall weakly aromatic and are not appreciably destabilized.

2) Synthesis of and Structural Characterization of a Heterocyclic Heptacene

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[20] Schleyer, P. V. R.; Manoharan, M.; Wang, Z. X.; Kiran, B.; Jiao, H.; Puchta, R.; Hommes, N. J. R. v. E. *Org. Lett.* **2001**, 3, 2465-2468.

[21] (a) Kutzelnigg, W. *Isr. J. Chem.* **1980**, 19, 193-200. (b) Pipek, J.; Mezey, P. G. *J. Chem. Phys.* **1989**, 90, 4916-4926. (c) Malkin, V. G.; Malkina. O. L.; Casida M. E.; Salahub, D. R *J. Am. Chem. Soc.* **1994**, 116, 5898-5908.

[22] (a) Corminboeuf, C.; Heine, T.; Weber, J. *Org. Lett.* **2003**, *5*, 1127-1130 (b) Moran, D.; Manoharan, M.; Heine, T.; Schleyer, P. v. R. *Org. Lett.* **2003**, *5*, 23-26. (c) Heine, T.; Schleyer, P. v. R.; Corminboeuf, C.; Seifert, G.; Reviakine, R.; Weber J., *J. Phys. Chem. A,* **2003,** 107 (33), 6470 -6475.

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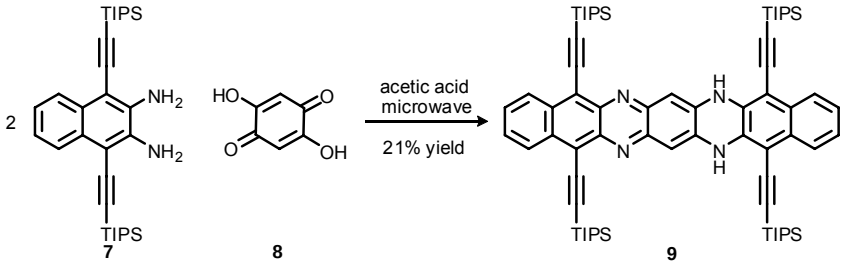
An important and largely unsolved question is the preparation of larger heteroacenes. At the moment there are no larger than heteropentacene derived materials structurally characterized. We found that by simple acid catalyzed condensation of an excess of **7** with **8** under microwave irradiation furnishes the red-fluorescent tetrayne **9**. From ^{1}H NMR and ^{13}C NMR spectra we conclude that **9** did form and not its dehydrogenated, fully aromatic congener, in line with the results we have obtained for the diazatetracenes. While the yield of this reaction is not particularly high, it is easy to make **9** on a multi-100-mg scale under those conditions. We were able to grow a suitable specimen for single crystal X-ray structure determination (see Figures 4,5). As the molecules of **9** are disordered in the solid state, the structure representation displays all four heterocyclic nitrogen atoms to carry hydrogen substituents. This, however is only due to the observed disorder and not a sign that the fully reduced material forms.



7 **8** **9**

***Scheme 3*.** Synthesis of the heteroacene **9**

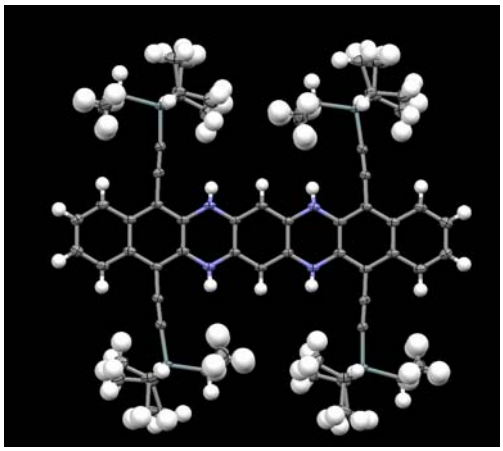


Figure 4. Single crystal structure of **9**

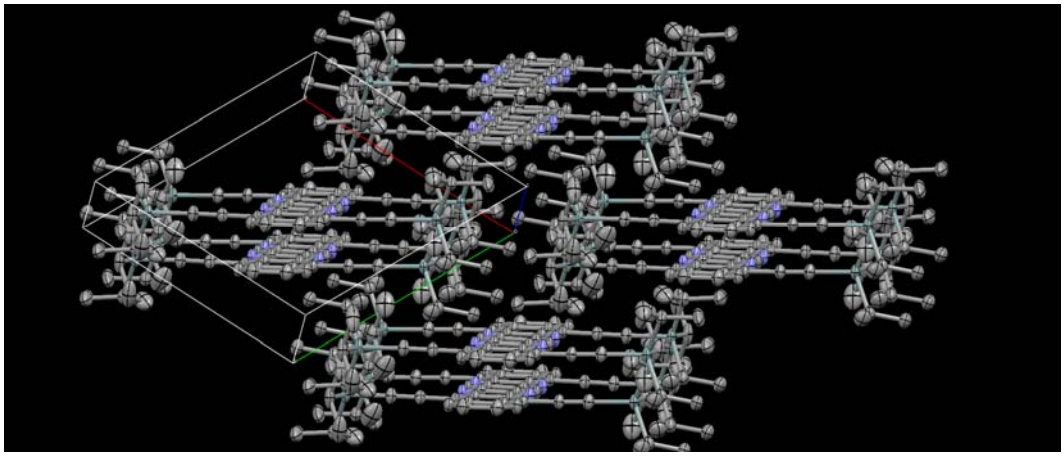
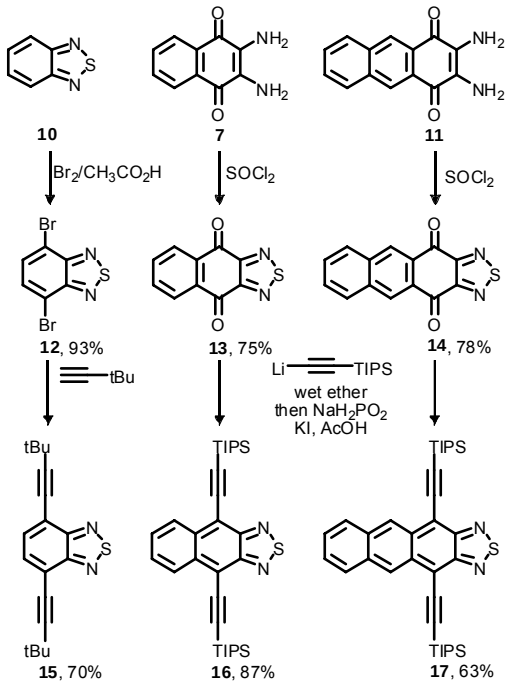


Figure 5. Packing of **9** in the solid state.



Scheme 3. Synthesis of the heteroacenes **15-17**

It was of interest to investigate the solid state packing of **9**, as it will be of interest in organic electronic applications. Interestingly, the compound packs in a way that separates pairs of heteroheptacenes by the bulky triisopropylsilyl groups. At the moment we investigate the electric properties of **9** in collaboration with Prof. Kippelen at the EE department at Gatech. We plan to make the corresponding nonacene derivatives by the same approach and plan to study its packing to see if the longer π-systems will display increased electronic interactions and a packing behavior similar to that seen for the larger acenes.

3) Synthesis and Property Evaluation of Larger Acenothiadiazoles

As there is great interest in organic n-semiconductors, the synthesis of *any* larger heteroacene and larger heterocyclic acene-like species is attractive. As the benzothiadiazole group is a powerfully electron withdrawing group, we were interested in the synthesis, crystal structures and property evaluation of the larger benzo, naphtho and anthraceno-substituted annelated benzothiadiazoles **15-17**. Scheme 3 displays the synthesis of these species, which are all easily available. In the case of **10**, bromination followed by Sonogashira coupling furnishes **15**, while**16** and **17** are synthesized starting from the diamines **7** or **11**. Reaction with thionyl chloride creates the benzothiadiazole ring and gives **13** and **14**. The quinone unit is then transformed into the 1,4-bisethynyl species by reaction with lithium(triisopropylsilylacetylide), hydrolysis by wet ether and dehydroxylation by a mix of NaH_2PO_2 and KI in acetic acid. The formed diethynylated benzothiadiazoles **15**-**17** are well soluble in hexanes and dichloromethane or chloroform and can be crystallized from these solvents to give specimen suitable for X-ray structure analysis.

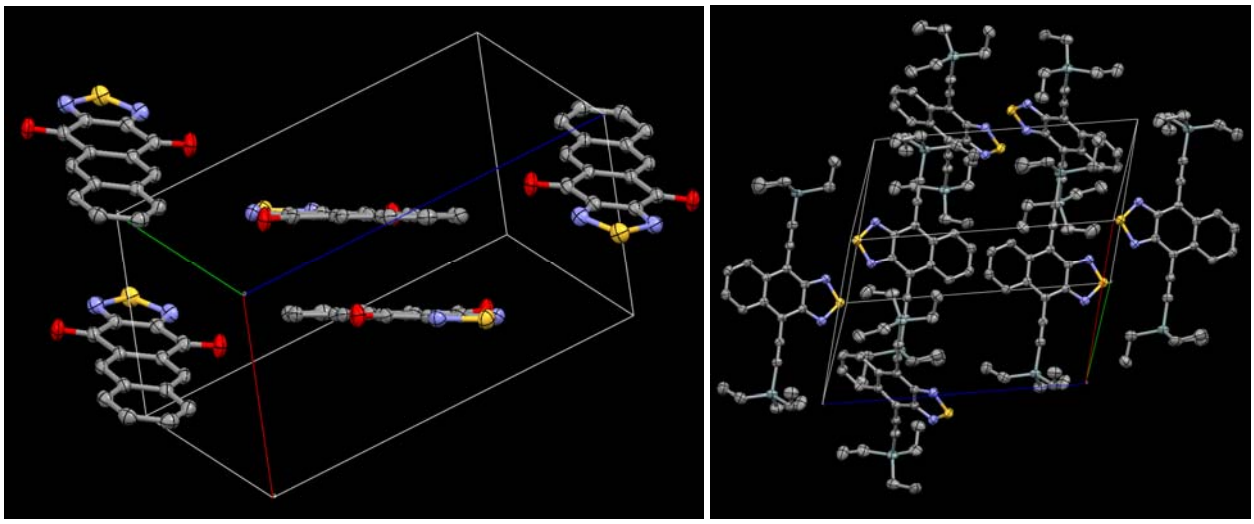


Figure 6. Packing of **14** in the solid state (Left). Packing of **16** in the solid state (Right).

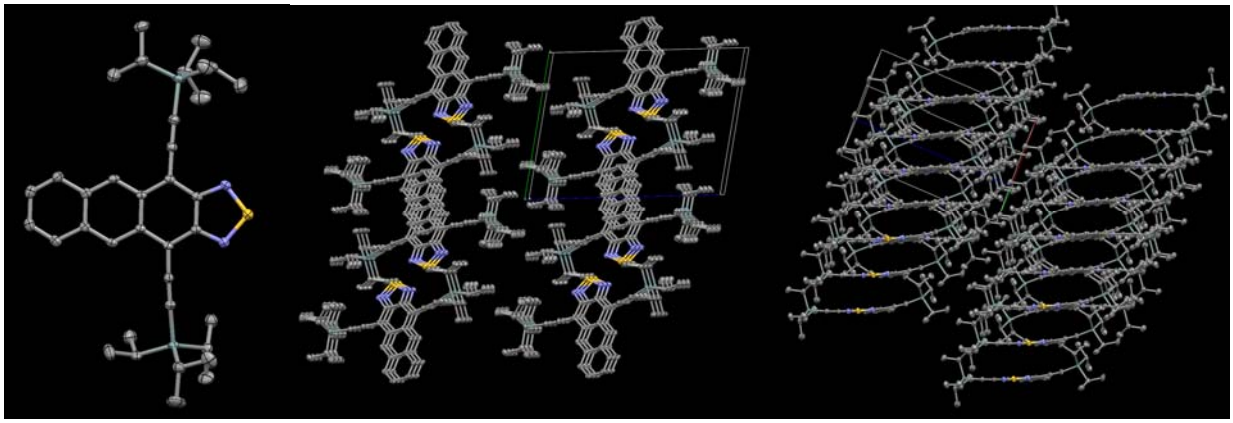


Figure 7. Packing of **17** in the solid state.

Figures 6-7 display the packing of **14**, **16** and **17** in the solid state. In the case of **14** the thiadiazole-quinone, there are no unusual packing motifs visible, and the molecules pack in pairs, but there is no one or two-dimensional stack motif or a motif that would suggest that this material would be a good n-semiconductor. Surprisingly, the thiadiazole units do not form their typical dimeric $(SN)_2$ arrangement.

In the case of **16** this supramolecular four ring (Figure 6) does form, and the thiadiazole rings form a dimeric pair but the packing of the arene units is such that there is no good overlap of adjacent π-systems of these species exist. However, in the larger congener, **17**, the packing is similar to that of the diethynylacenes described by Anthony et al.[3,4,16] In this case the π-faces (Figure 7) overlap significantly and at the same time the dimeric benzothiadiazole packing motif is well developed. The compound **17** is easily reduced at -0.7 and -1.3 V, suggesting that it will be an excellent n-semiconductor. The Uv-vis and emission spectra in solution and thin films are also shown in Figure 9. Upon going into the solid state, the fluorescence disappears and the color deepens to blue black as is witnessed by the absorption shift from 656 nm to 666 nm and the very significant broadening. This material does absorb from 450 down to 750 nm and may be therefore an excellent candidate for applications in photovoltaic applications. At the moment we collaborate with Profs. Kippelen and Marder and their groups to evaluate the electric and the solid state semiconducting properties of the exciting compound **17** and its derivatives and push applications of **17** in photovoltaics.

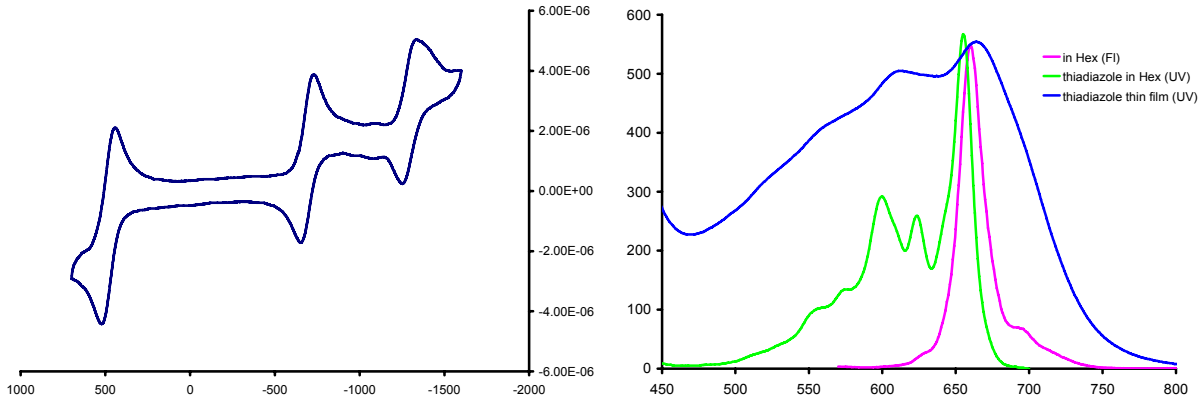


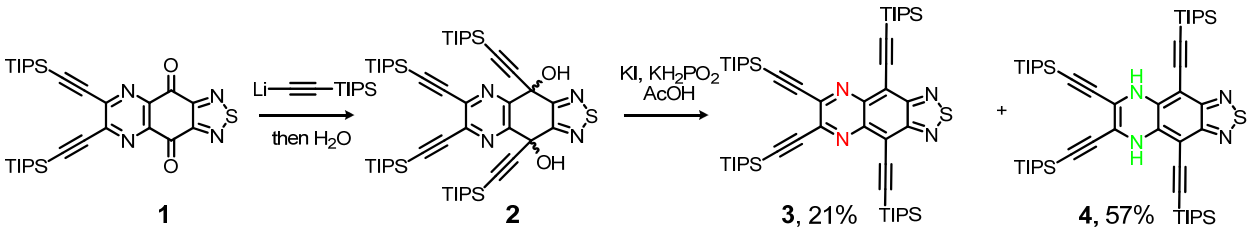
Figure 8. Left: Cyclic voltammogram of **17** in THF. Peaks at -0.69 and -1.28 V are due to reversible reduction of the benzothiadiazole unit. The peak at +0.5 V is due to the addition of ferrocene as reference. Right: UV-vis and emission spectra of **17** in solution and in the solid state.

Heteroacenes ($ 390,000, 03/2006 – 03/2009), CHE 0548423

Uwe Bunz PI

I. Aromaticity and Antiaromaticity in Larger Polycyclic Heterocycles

During this grant period we have synthesized and investigated a series of larger polycyclic N-heterocycles and their N,N-dihydrogenated and formally antiaromatic congeners and examined these pairs of aromatic/antiaromatic targets by spectroscopic and quantum chemical calculations, (collaboration Prof. Schleyer, U of Georgia, Athens). We developed a synthetic route to **3** as precursor to *ortho*-diamine modules for the construction of heteroacene-structures. The synthesis of **3** is straightforward, however, reduction of **2** furnishes **3** in only 21% yield, with the reduced **4** (NH-stretch at 3401 cm^{-1}) being the main product; **4** is Hückel-antiaromatic and expected to be unstable and non-persistent. An X-ray crystal structure (Figure 2) proves that **4** is planar with N-H units present. Oxidation of **4** to **3** is facile via spontaneous air oxidation in solution.



Scheme 1. Synthesis of the aromatic and the antiaromatic peralkynylated heterocycles **3** and **4**.

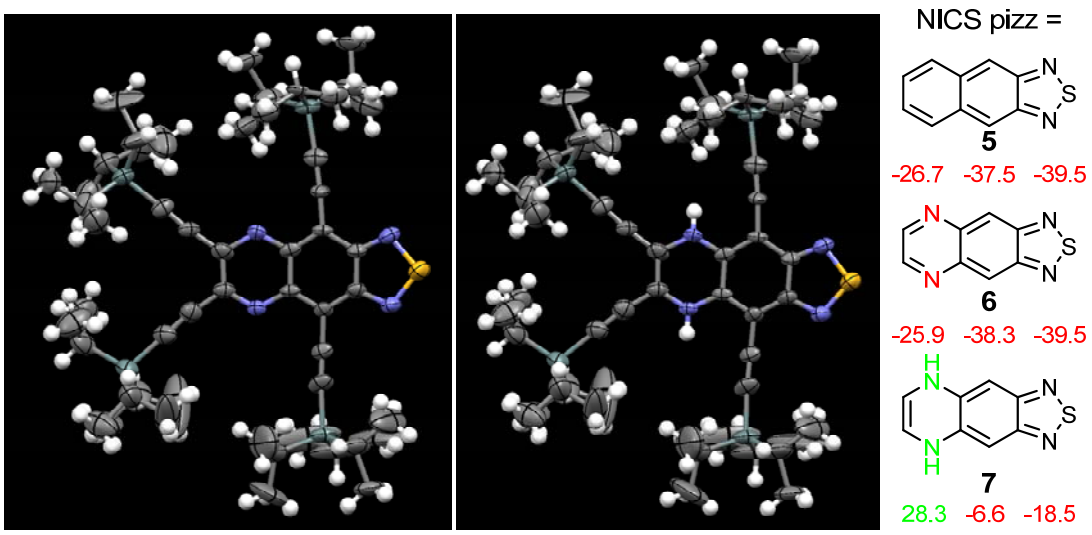


Figure 1. Single crystal X-ray analysis of **3** and **4** (left); NICS values of **5-7** (collaboration Schleyer, right).

Aromaticity gauges are a) Hückel-rule: 4n+2 π-perimeters are aromatic, b) thermodynamic measures: reduction of benzene is endothermic, c) magnetic properties: rings with large negative NICS (nucleus independent chemical shifts) values are aromatic. We computationally investigated the hydrogenation of **6** + H_2 → **7** and determined the NICS values of the models **6** and **7**: the heterocycle **6** is aromatic. In **7** the dihydropyrazine ring is substantially antiaromatic, and the aromaticity of the two other rings is significantly attenuated.

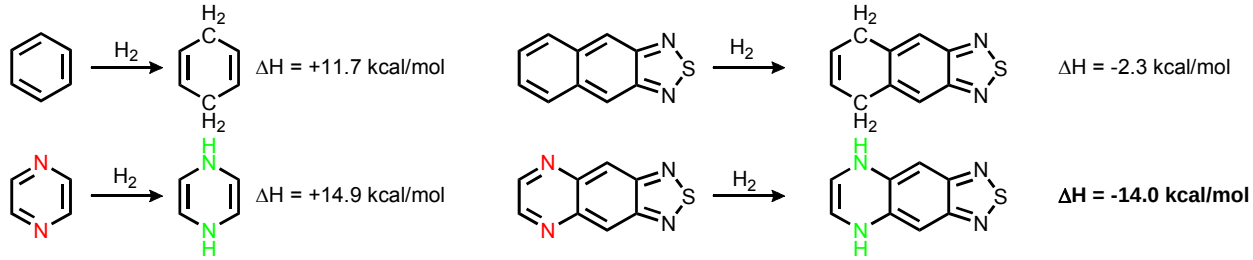
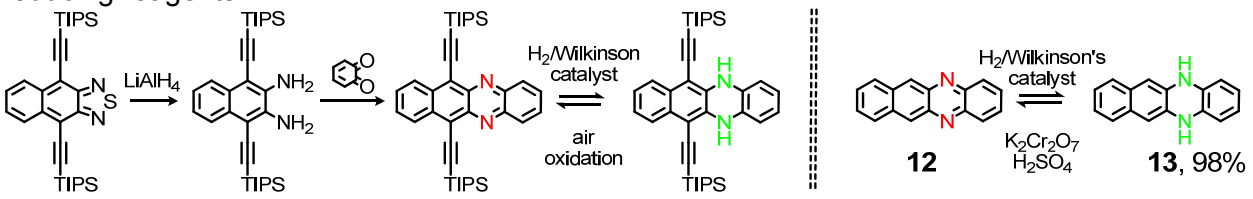


Figure 2. Heat of hydrogenation (B3LYP 6-311+G**//B3LYP 6-311+G**, ZPE).

However, according to quantum chemical calculations, hydrogenation of **6** into **7** is exothermic (Figure 2), unlike the hydrogenation of benzene or pyrazine. Donor-acceptor effects do not play a large role in the stabilization of the antiaromatic species. The syntheses of **10-13** is shown in Scheme 2 while **12** and **13** were first prepared by Hinsberg in 1901[1,2] but did not attract much attention. The aromatic/antiaromatic redox-switching between **10/11** and **12/13** is facile, occurs with high yields and can be repeated multiple times, suggesting their use as novel reducing reagents.



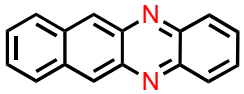
8 **9**, 98% **10**, 63% **11**, 98% **12** **13**, 98%

Scheme 2. Synthesis of the aromatic diazatetracene derivative **10** and its N,N-bishydrogenated congener **11** (left). Interconversion between **12** and **13**.

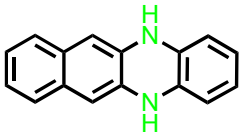
The compound **13** can be crystallized from DMF, but re-oxidizes to **12** in DMSO, while **11** oxidizes to **10** in air. Quantum chemical calculations (B3LYP/6-311+G**//B3LYP/6-311+G**, ZPE correction) reveal that the hydrogenation of tetracene is less exothermic than the that of **12**, suggesting that its antiaromatic character does not impart significant destabilization.

12 + $H_2 \rightarrow$ **13**	ΔH_H = –20.8 kcal/mol	(eq. 1)
Tetracene + $H_2 \rightarrow$ 5,12-Dihydrotetracene	ΔH_H = –15.0 kcal/mol	(eq. 2)

To evaluate the issue of aromaticity further we performed NICS calculations on **12** and **13** (Figure 4); **12** is aromatic according to NICS calculations. Its aromaticity is mostly determined by the local contributions of the participating rings. Aromaticity is a localizing force – on a per ring basis – remote contributions are small. In the case of the Hückel-antiaromatic **13** all of the "remote" contributions are of antiaromatic nature, while the local contributions of rings A, C and D betray them as aromatic with negative NICS values. The B-ring is antiaromatic. The total LMO and CMO data display the overall aromaticity of the rings and the molecule. When comparing the global NICS values of **12** with those of **13**, one can conclude that **13**'s aromaticity is reduced. Surprisingly the antiaromatic character has a delocalizing effect on the system, while the aromatic character is mostly confined to specific rings. While counter-intuitive, larger antiaromatic systems such as **13** are *less* destabilized than smaller ones, while for aromatic systems the reverse is true, as expressed in the Clar rule.[3] It might therefore be more useful to inspect aromaticity of a molecule on a per-ring basis and less of a global property.



12

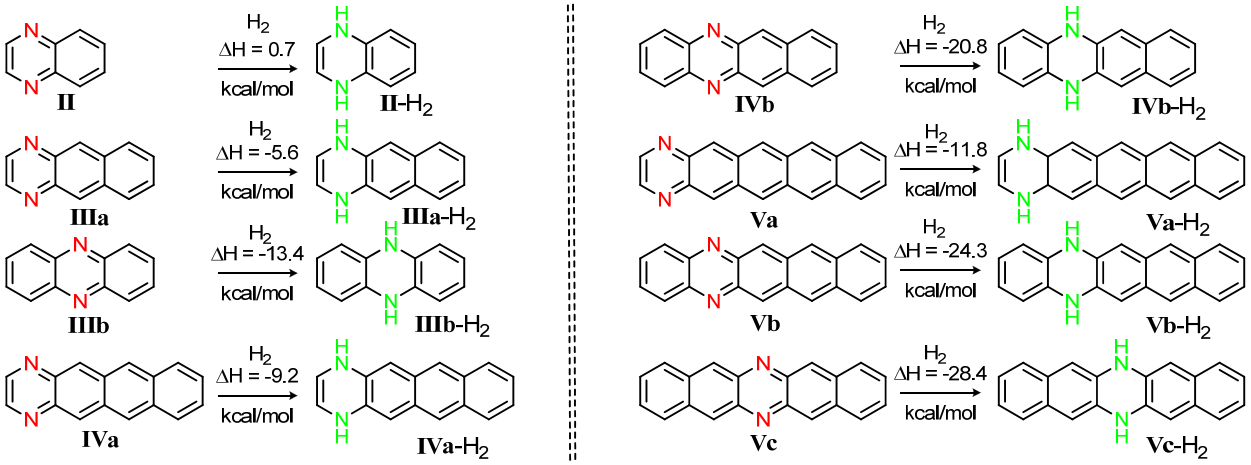


13

LMO	Remote	-2.0	-3.8	-3.6	-2.8	$\Sigma_{NICS(0)zz}$ = -12.2	7.9	15.1	2.1	15.7	$\Sigma_{NICS(0)zz}$ = 40.8
	Local	-28.0	-39.1	-38.2	-27.9	$\Sigma_{NICS(0)zz}$ = -133.2	-35.1	-29.9	27.6	-33.4	$\Sigma_{NICS(0)zz}$ = -70.8
	Total	-30.0	-42.9	-41.8	-30.4	$\Sigma_{NICS(0)zz}$ = -145.4	-27.2	-14.8	29.7	-17.7	$\Sigma_{NICS(0)zz}$ = -30.0
CMO	Total	-30.0	-42.5	-41.1	-30.1	$\Sigma_{NICS(0)zz}$ = -144.0	-26.8	-14.2	31.3	-16.7	$\Sigma_{NICS(0)zz}$ = -25.9

Figure 3. IGLO-LMO (localized molecular orbital) and GIAO-CMO (canonical molecular orbital) NICS(0)πzz of **12** (left) and **13** (right) computed at PW91/IGLO-III//B3LYP/6-311+G**. "Local" refers to the π LMO contributions of individual localized double bonds and lone pairs associated with the designated individual rings. "Remote" refers to the remaining π MO contributions. The sum of the remote and local total LMO contributions closely matches the CMO.

In a further collaboration with Prof Schleyer, we have investigated the energetic issues surrounding the hydrogenation of diazaacenes and compared the resonance energies and the extra cyclic resonance energies (ECREs) of the different aromatic and formally antiaromatic species **II-V** (Scheme 3).



Scheme 3. Hydrogenation of the diazaacenes **II-V**. The thermochemical values are calculated using B3LYP-6311G**// B3LYP-6311G** with ZPE correction.

In Figure 4 the RE and the ECRE of these systems are displayed, and the trends show that the larger diazaacenes are thermodynamically less stable than their hydrogenated congeners. This is explained as a consequence of the breakup of one large aromatic system into two smaller ones and is entirely in line with the Clar rule, stating that compounds with more isolated benzene rings are more aromatic. At the same time, the antiaromatic character of the central ring decreases with increasing size of the heteroacene. Antiaromaticity is a delocalizing force in the sense that larger antiaromatic rings experience less of a destabilization than smaller ones. The performed magnetic calculations (NICS) suggest that the dihydropyrazine rings in **II**-H_2-**V**-H_2 are magnetically antiaromatic (Figure 3), which leads to a significantly reduced overall aromaticity of the systems. However, compounds like **III**-H_2-**V**-H_2 are clearly not overall antiaromatic, they only show reduced aromaticity, but are thermodynamically stabilized and according to our (and other researchers) experimental findings fully persistent even though they are 4n-pi-systems and therefore Hückel antiaromatic. Figure 4 shows the pertinent details.

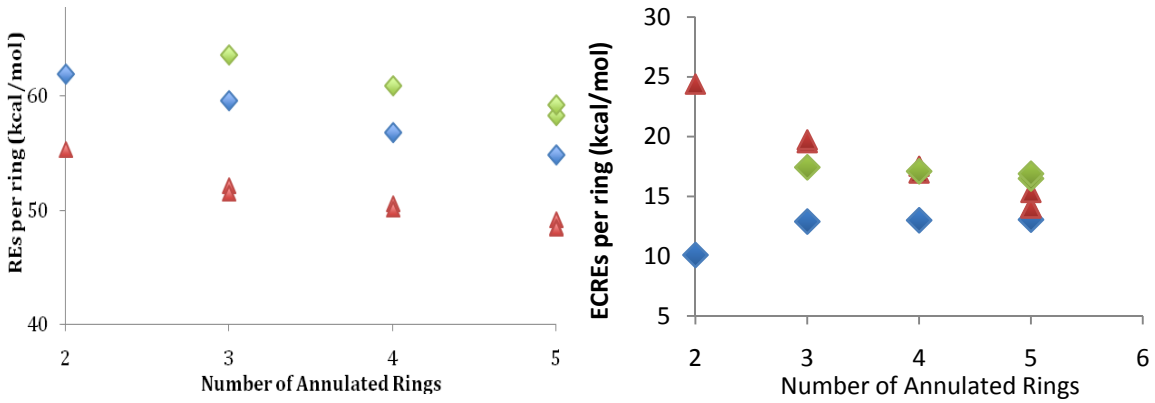


Figure 4. (left) Resonance energies (REs) per ring vs. the number of annulated rings (N = 2 to 5) for the dihydroazaacenes (**II**-H_2 to **V(a-c)**-H_2; blue and green rhomboids) and diazaacenes (**II** to **V(a-c)**; red triangles). The 1,4-dihydroazaacenes (**II**-H_2, **IIIa**-H_2, **IVa**-H_2 and **Va**-H_2) are in blue; their isomers with reduced inner rings (**IIIb**-H_2, **IVb**-H_2 and **V(b-c)**-H_2 are in green. All BLW data are computed at the B3LYP/6-31G* level. (right) Extra cyclic resonance energies (ECREs) per ring vs the number of annulated rings (N = 2 to 5) for dihydroazaacenes (**II**-H_2 to **V(a-c)**-H_2; blue and green rhomboids) and diazaacenes (**II** to **V(a-c)**; red triangles). The 1,4-dihydroazaacenes (**II**-H_2, **IIIa**-H_2, **IVa**-H_2 and **Va**-H_2; blue rhomboids) can have only one Clar ring, and thus have less ECRE per ring compared to their isomers (**IIIb**-H_2, **IVb**-H_2 and **V(b-c)**-H_2; green rhomboids) with two Clar rings. All BLW data are computed at the B3LYP/6-31G* level.

As we are interested in the electronic properties of the diazaacenes and their hydrogenated congeners, we obtained Uv-vis and emission spectra for **10** and **11** (Figure 5). Upon reduction from **10** to **11** the absorption and emission maxima shift into the blue. This is surprising as – according to Hückel theory– formally antiaromatic systems should have smaller band gaps than their aromatic congeners. In **11** reduction led to a larger destabilization of the LUMO than of the HOMO as compared to **10** according to DFT calculations, explaining the observed features.

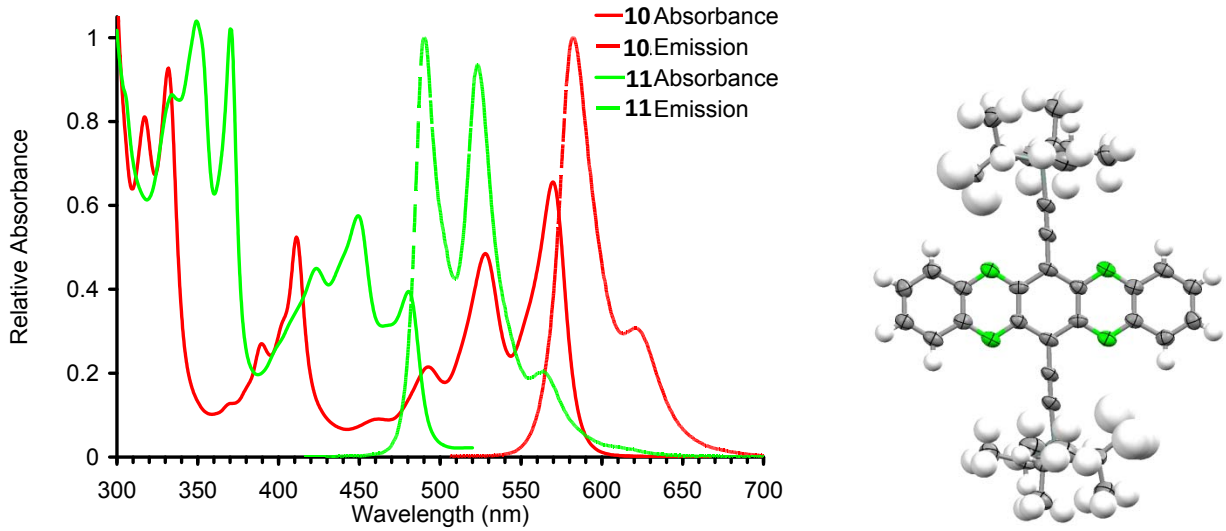


Figure 5. UV-vis and emission spectra of **10** and **11**in dichloromethane (left) and ORTEP of **16**.

II. Synthesis of larger and different heterocyclic systems.

As pentacene is a most useful OS for thin film transistors,[4] the synthesis of its N-heterocyclic derivatives is of interest. We have developed a set of building blocks that gives an array of different N-heterocyclic targets. We discovered that benzothiadiazole-annelated acenes **23,24**, versatile precursors for *ortho*-diamines, are fascinating targets in their own right, as the benzothiadiazole unit a) significantly red-shifts absorption and emission and b) displays a solid-state packing motif in which intermolecular S-N interactions modulate the packing.

a) Synthesis: Attaching alkynes to pentacene stabilizes the arene,[5] manipulates packing and increases solubility and processability. Conversely, pyrazine-type substitutions in pentacene, are only sparsely described.[6] Starting from **14** (Figure 6)[7] alkynylation followed by dehydroxylation[8] affords **15**, then **16** by MnO_2 the first characterized tetraazapentacene.[9] *An X-ray crystal structure of **16** is shown in Figures 5 and 6*. The arenes are packed in a parallel, nearly coplanar fashion. We are investigating the electrochemistry and film-forming properties of **16**.

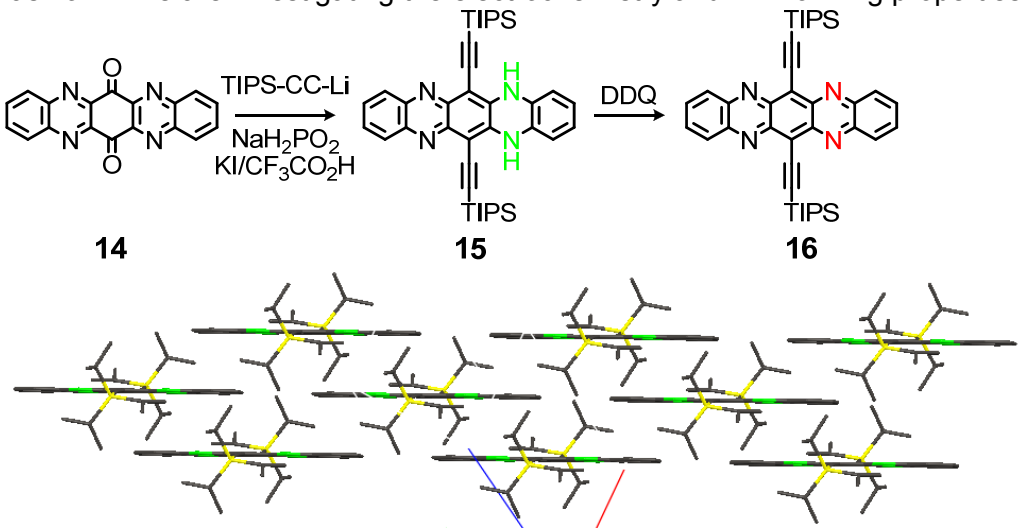
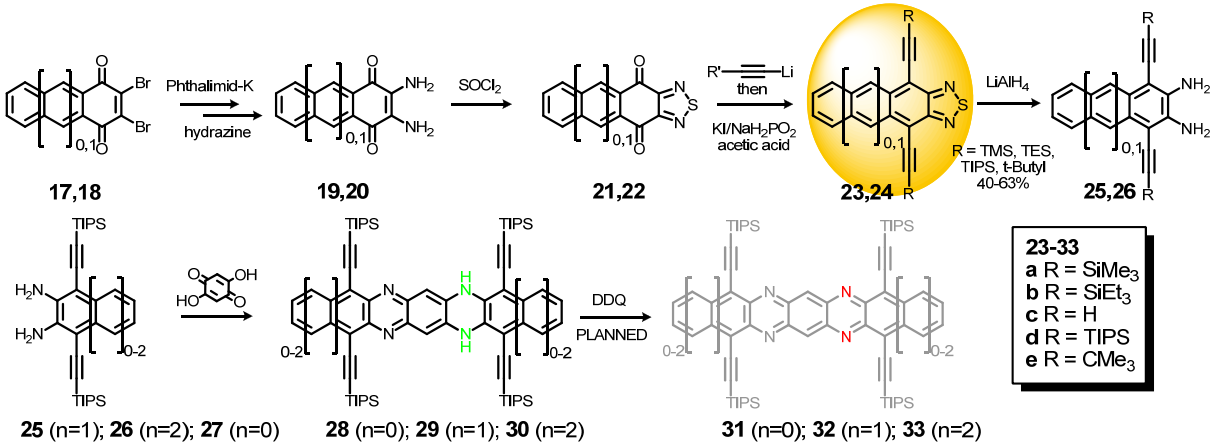


Figure 6. Synthesis of **15** and **16**, and packing of **16**. The layers are separated by 3.4 Å and there is significant cofacial overlap.



Scheme 4. Synthesis of the larger benzothiadiazoles and the larger heteroacenes.

Scheme 4 (top) displays the synthesis of the benzothiadiazoles **23** and **24**. Starting from **17** or **18** substitution with phthalimide-potassium followed by hydrazinolysis and reaction with thionyl chloride furnishes the quinones **21** and **22**, which are alkynylated and reduced to give **23**

and **24**; lithium aluminum hydride reduces these into **25** and **26**, which together with **27** are useful starting materials for the synthesis of **28-30**. Synthesis of **28** and **29** is facile, a single crystal structure of **29** was obtained. At the moment we are oxidizing **28-30** into **31-33**.

*b) Solid-State Structures of **24a,b** (R= $SiEt_3$ and R = $SiMe_3$):* The spectroscopic properties of **24a,b** are attractive as the materials are black in the solid state and have an emission at 700 nm in dichloromethane and absorbs from 500-700 nm in the typical acene-type, vibronically structured bands. The two benzothiadiazoles **24a,b** differ only in their silyl protecting group, yet their packing is different. Both form stacks with intrastack distances of 3.4 Å. In **24b** these stacks are connected to each other by supramolecular S-S interactions via four membered (-S-N-)$_2$-rings that connect stacks to each other. The lateral distance between two arenes is 3.17 Å, shorter than the van der Waals distance between nitrogen and sulfur promising to support charge carrier transport; **24a,b** may turn out to be attractive alternatives to pentacene. Their solution optical properties are similar to that of pentacene and we plan to fabricate thin films of high quality from which we will obtain charge carrier mobilities in collaboration with Prof. Kippelen. At the moment however the preparation of suitable thin films is the greatest challenge due to delamination and pinhole formation of these materials on glass or ITO.

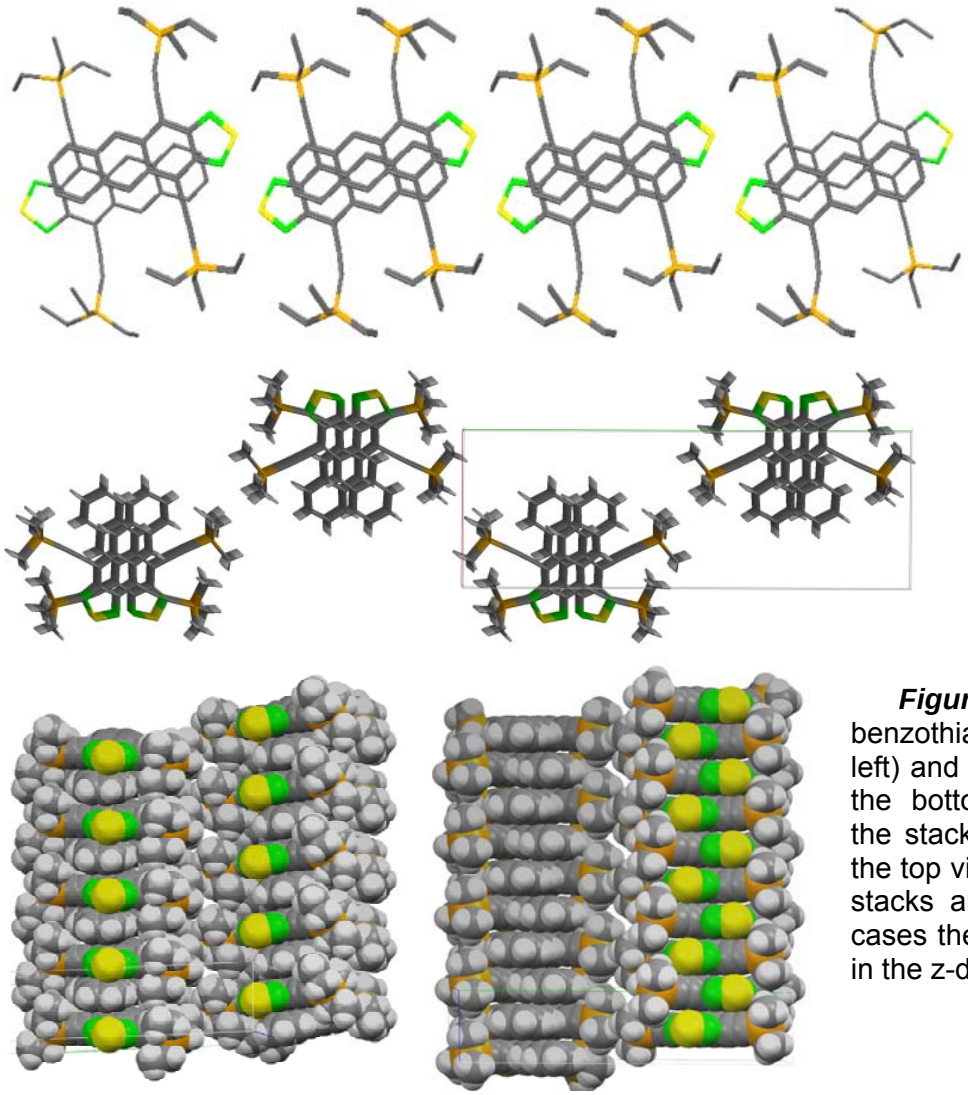


Figure 7. Packing of the benzothiadiazoles **24b** ($SiEt_3$, left) and **24a** ($SiMe_3$, right). At the bottom the formation of the stacks is displayed, while the top view pinpoints how the stacks are arranged. In both cases the intrastack distances in the z-direction are 3.4 Å.

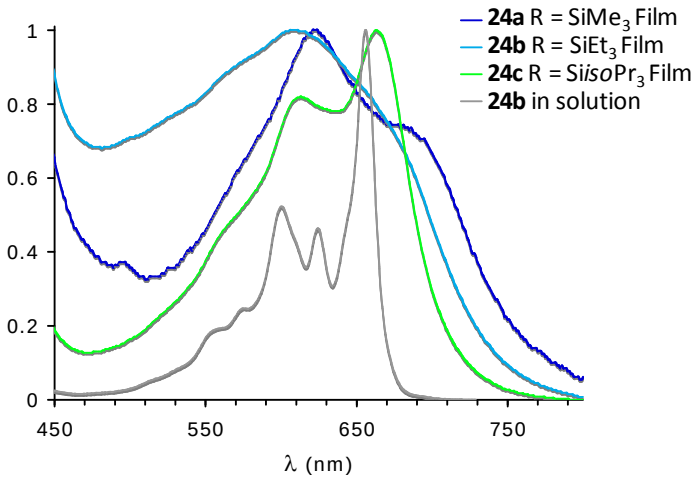


Figure 8. Micrograph state UV-vis spectra of **24a-c** in the solid state as thin drop-cast films. For comparison the spectrum of **24b** in solution is displayed in grey.

Figure 8 displays the thin film solid state UV vis spectra of **24a-c** and as comparison the spectrum of **24b** in solution. As shown in Figure 7, the interactions between the anthraceno-thiadiazole units are reflected in a red-shifted absorption of **24a-c.** As one would expect, **24c** with the bulky TIPS groups experiences the least red-shift, while the columns of **24a** or **24b** suggest an increased interaction of the pi-systems of these thiadiazoles in the solid state. The general tuneability of these interactions in the solid state makes these species quite attractive as potential materials for either active layers in thin film transistors or photovoltaic cells.

To show that the formed heteroacenes are potentially useful in organic electronics, we investigated their film forming properties on quartz slides. On untreated quartz slides globs of materials developed, however, when trimethylsilyl-coated glass was used, slow evaporation of a solution of **10** led to the formation of small 10-200 μm large rhombohedral crystals (Figure 8). AFM delineates that these crystals are approximately 2-3 μm thick and have a very smooth surface that is studded with 2-3 μm large and 1-2 nm high triangular features. Other than these features, the surface of the crystals is virtually flat and should allow to use these rhombohedra in single crystal thin film transistors.

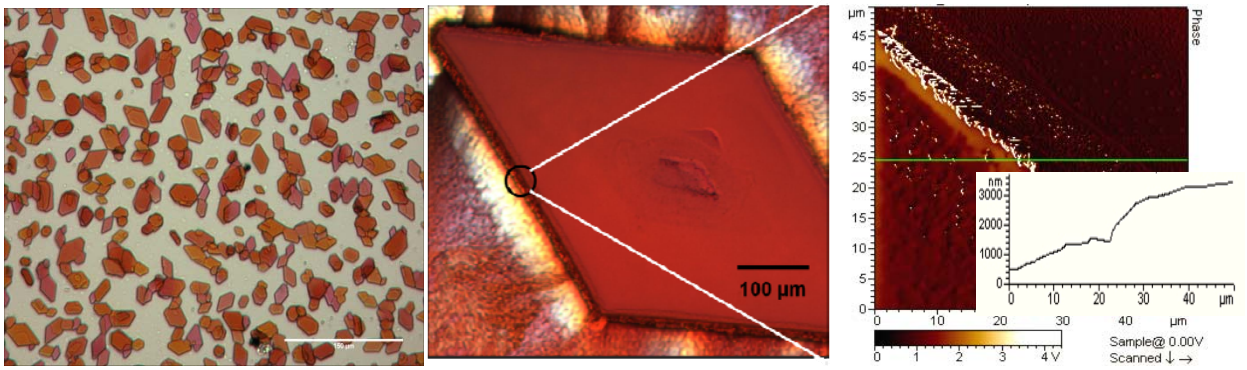


Figure 9. Micrograph of small rhombohedral crystals of diazatetracene **10** on HDMS-treated hydrophobic quartz glass (left). AFM of a somewhat larger rhombohedral single crystal of **10** and a close up view of the corner. The crystals are approximately 3 microns thick.

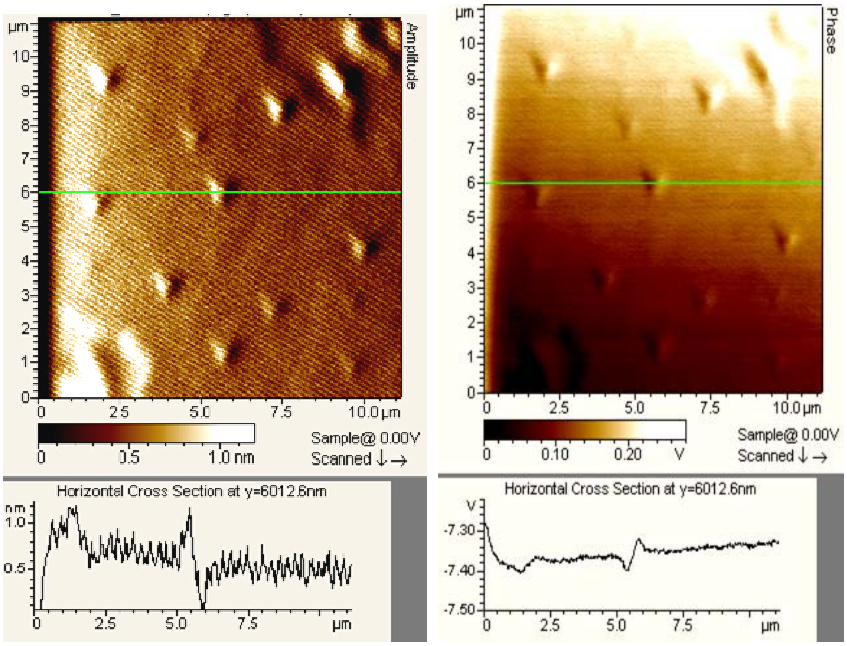


Figure 10. Hight and phase contrast AFM of a rhombohedral crystal of **10**. The crystalline faces are flat but display small triangular features that are approximately 1.5 nm in height.

In collaboration with Prof. L. M. Tolbert and Prof. C. L. Henderson we currently investigate the directed crystal growth of such rhombohedra on indium tin oxide and SiO_2-passivated silicon to extract their electrical properties. In addition we are currently attempting the growth of such small scale crystals on quartz surfaces that have a hydrophobicity contrast, which we will use to direct the loci of crystal growth. The experience that we will have obtained from these experiments will be used to fabricate thin film transistors using our N-heteroacenes.

Conclusions

This project has been both challenging as well as rewarding. While the syntheses of the larger N-heteroacenes look quite easy on paper, very often the yields of the reactions are relatively low and a significant amount of optimization and the use of novel or unusual reagent combinations is necessary. A particularly intriguing issue was the development of reduction of dihydro-aceno-diols into their acenes. The classic methods such as tin chloride reduction did not give any product in the case of these highly electron withdrawing substrates, however a combination of phosphite and iodide in strong organic acids does the job satisfactorily to make the larger alkynylated heteroacenes. It seems that this method is generally applicable.

On the materials side we have made the first soluble and processible azapentacenes and a series of novel enlarged acenothiadiazoles and have developed a building block approach for the construction of larger aromatic linearly fused heterocycles.

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